

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 12-04-2016		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Feb-2015 - 31-Jan-2016	
4. TITLE AND SUBTITLE Final Report: Singlet-Fission-Sensitized Hybrid Thin-Films For Next-Generation Photovoltaics.			5a. CONTRACT NUMBER W911NF-15-1-0040		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 106012		
6. AUTHORS Tang, Ming Lee			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of California - Riverside 200 University Office Building  Riverside, CA 92521 -0001			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66355-MS-REP.4		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This grant enabled the acquisition of equipment for the fabrication of organic and nanocrystal based photovoltaic (PV) devices by creating rationally designed organic-inorganic hybrid systems that exploit the unique multi-excitonic properties of both types of materials. A suite of equipment associated with electronic spectroscopy and PV device fabrication and characterization was acquired. For spectroscopy, NIR laser diodes and a camera capable of ultrafast photoluminescence in the near infra-red (NIR) was procured. For PV fabrication, a glovebox with thermal evaporators and a spin coater was constructed. In order to characterize PV devices, a solar simulator					
15. SUBJECT TERMS singlet fission, nanocrystal, triplet, hybrid, photovoltaic					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Ming Tang
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 951-827-5964

## Report Title

Final Report: Singlet-Fission-Sensitized Hybrid Thin-Films For Next-Generation Photovoltaics.

### ABSTRACT

This grant enabled the acquisition of equipment for the fabrication of organic and nanocrystal based photovoltaic (PV) devices by creating rationally designed organic-inorganic hybrid systems that exploit the unique multi-excitonic properties of both types of materials. A suite of equipment associated with electronic spectroscopy and PV device fabrication and characterization was acquired. For spectroscopy, NIR laser diodes and a camera capable of ultrafast photoluminescence in the near infra-red (NIR) was procured. For PV fabrication, a glovebox with thermal evaporators and a spin-coater was constructed. In order to characterize PV devices, a solar-simulator, semiconductor parameter analyzer and associated components to measure current density-voltage curves, external and internal quantum efficiencies were obtained.

---

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
02/04/2016	1.00 Zhiyuan Huang, Xin Li, Melika Mahboub, Kerry M. Hanson, Valerie M. Nichols, Hoang Le, Ming L. Tang, Christopher J. Bardeen. Hybrid Molecule–Nanocrystal Photon Upconversion Across the Visible and Near-Infrared, Nano Letters, (08 2015): 0. doi: 10.1021/acs.nanolett.5b02130
02/04/2016	2.00 Zhiyuan Huang, Xin Li, Benjamin D. Yip, Justin M. Rubalcava, Christopher J. Bardeen, Ming L. Tang. Nanocrystal Size and Quantum Yield in the Upconversion of Green to Violet Light with CdSe and Anthracene Derivatives, Chemistry of Materials, (11 2015): 0. doi: 10.1021/acs.chemmater.5b03731
04/11/2016	3.00 Zhiyuan Huang, Duane E. Simpson, Melika Mahboub, Xin Li, Ming L. Tang. Ligand enhanced upconversion of near-infrared photons with nanocrystal light absorbers, Chem. Sci., ( 2016): 0. doi: 10.1039/C6SC00257A
<b>TOTAL:</b>	<b>3</b>

**Number of Papers published in peer-reviewed journals:**

---

**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
-----------------	--------------

**TOTAL:**

Number of Papers published in non peer-reviewed journals:

---

(c) Presentations

Zhiyuan Huang (4th year graduate student) presented a poster and a talk at the 251st ACS National Meeting in San Diego, March 2016:

Talk:  
INOR 1286: Hybrid molecule-nanocrystal photon upconversion across the visible and near-infrared  
Thu, Mar 17 2016  
Publication Number: 1286

Poster:  
INOR 283: CdSe/CdS core-shell nanocrystal sensitizers for molecule-nanocrystal photon upconversion  
Sun, Mar 13 2016  
Publication Number: 283

Number of Presentations: 2.00

---

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
-----------------	--------------

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

---

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
-----------------	--------------

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

---

(d) Manuscripts

Received      Paper

TOTAL:

Number of Manuscripts:

---

Books

Received      Book

TOTAL:

Received      Book Chapter

TOTAL:

Patents Submitted

Acene-based transmitter molecules for hybrid molecular-nanocrystal photon upconversion

---

Patents Awarded

---

Awards

2016 Chinese American Faculty Association of Southern California (CAFA) Faculty Development Grant was awarded to Ming Lee Tang (PI)

---

---

### Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

---

### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

---

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

---

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

---

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

---

### Names of Personnel receiving masters degrees

<u>NAME</u>
<b>Total Number:</b>

---

### Names of personnel receiving PhDs

<u>NAME</u>
<b>Total Number:</b>

---

### Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

---

### Sub Contractors (DD882)

### Inventions (DD882)

### Scientific Progress

This grant has enabled the Tang laboratory to establish itself as a diverse nanofabrication and characterization facility incorporating a wet lab for chemical synthesis and manipulation, general spectroscopic and device characterization equipment. Specifically, this grant enabled device fabrication and characterization with the procurement of:

- Lorell spin-coaters in air and in glovebox; Harvard Apparatus syringe pumps
- Two thermal evaporators (Nexdep, Ångström Engineering) for metal and organic thin-film deposition integrated into (6 gloves) argon Inert Technology box. Separate evaporators are to prevent contamination of devices from residual organics.
- A separate device testing glovebox for the seamless transfer of devices in inert atmosphere in (2 gloves) argon box, equipped with a Keithley 2636B.
- There is a separate probe station in air (Signatone).
- Power Conversion Efficiency measurements for solar cells (Newport Solar Simulator).
- External Quantum Efficiency measurements from 400-1700nm (with Newport Tunable Light Source and detectors).

The instrumentation has facilitated the discovery last year, in this group, that photon upconversion is efficient using a combination of semiconductor nanocrystals (NCs) and conjugated organic molecules. The major discovery is that NCs can sensitize, or donate energy to molecular triplet states. Since this first demonstration, Baldo et al (Nature Photonics 2015) showed nanocrystal sensitized upconversion in thin film, while Castellano et al (Science 2016) directly confirmed molecular triplet sensitization from nanocrystal donors using transient absorption spectroscopy. Our hybrid molecule-nanocrystal photon upconversion technique makes use of 1) the large absorption coefficients of the nanoparticles and 2) their ability to extend into the near infrared (NIR). Both these characteristics, important for bioimaging, are unavailable simultaneously in existing lanthanide and molecule based photon upconversion

### Technology Transfer

**Equipment installed:**



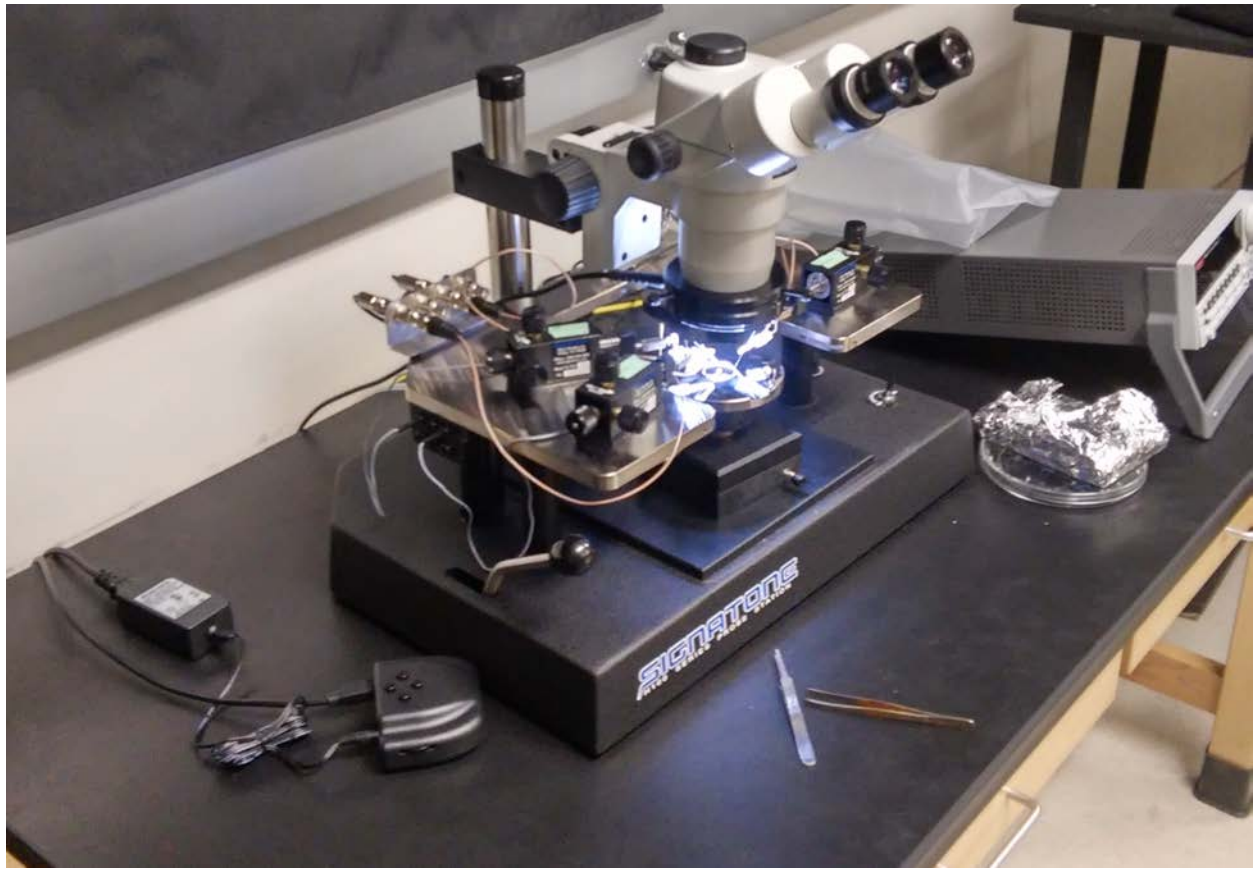
This is an eight-glove Innovative Technology glovebox that contains two thermal evaporators (Ångström Engineering), spin-coater, and a probe station for transistor and solar cell measurements. It is equipped with standard items like oxygen and moisture analyzers and purifiers, small and large antechambers. This glovebox has a spin-coater to coat substrates with nanoparticles or organic molecules, thus necessitating a special large reservoir to remove solvent within the glovebox. The thermal evaporator allows air-free manipulation of device substrates will be used to evaporate metal contacts on the hybrid film deposited on indium tin oxide (ITO). At ultra high-vacuum, the one on the left evaporates organics; the one on the right evaporates metal. Both evaporators are backed with a dry and turbopump. Substrate rotation and temperature control is included to control the crystallinity of thermally deposited organic semiconductors.



Proposal Number: 66355MSREP;

Agreement Number: W911NF1510040

Proposal Title: Singlet-Fission-Sensitized Hybrid Thin-Films For Next-Generation Photovoltaics.



Shown here is the Keithley 2636B semiconductor parameter analyzer that can source and measure 2-channels with 0.1fA resolution at 200V. Here, it is paired with the probe station that operates in air, a bare bones Signatone system with a vacuum chuck, microscope, light, triax probes, etc. The same setup is replicated in the glovebox above for air-free measurements, but both systems share the Keithley 2636B



This is the Bayspec near-infrared (NIR) spectrophotometer that collects the nanocrystal emission with a fiber. This grant also supported the purchase of other equipment like a Newport solar simulator, a 488 nm Coherent OBIS laser, a Stanford Research Systems Lock-In Amplifier 830m, a PicoHarp 300 and an InGaAs camera for NIR time-resolved experiments, various optical accessories from Newport and Thorlabs, as well as work by Physical Plants to install electrical and water cables.